

AD-A050 056 PRINCETON UNIV N.J. DEPT OF AEROSPACE AND MECHANICAL--ETC F/6 7/3  
OXIDATION KINETICS OF HYDROCARBON FUELS. (U)  
DEC 77 I GLASSMAN, F L DRYER, R J SANTORO AFOSR-74-2604  
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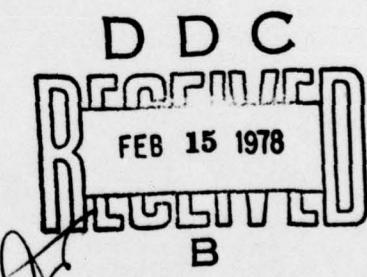
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Annual Report  
Air Force Systems Command  
Air Force Office of Scientific Research  
OXIDATION KINETICS OF HYDROCARBON FUELS

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Principal Investigators

AFOSR Grant No. 74-2604  
1 October 1973 to 30 September 1977

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1 December 1977

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## SUMMARY

Interest in improved performance and reduced emission characteristics of air breathing propulsion systems and a better understanding of plume problems has created a need for better definition of the coupled fluid mechanical and chemical kinetic processes which occur in these devices. Modeling of the necessary combustion chemistry in systems using hydrocarbon fuels is difficult because of the lack of adequate kinetic data. This study is designed to determine the overall reaction data expressions and the associated elementary kinetics for the oxidation reactions of these hydrocarbons.

A major conclusion of earlier work, besides the overall rate data reported, was that OH radical attack is not the primary mechanism contributing to the observed disappearance rates of methane (and other aliphatics through hexane) in high temperature, oxygen rich combustion. Experimental data obtained using the  $\text{CO}/\text{H}_2\text{O}/\text{O}_2$  reaction seeded with small amounts of hydrocarbon suggest that some reaction is reforming the initial fuel at a fast rate in comparison to hydrogen abstraction by hydroxyl radicals during the oxygen rich oxidation. There does not appear to be simple overall rate expression of the form

$$\frac{-d[RH]}{dt} = k_{ov} [RH]^a [O_2]^b$$

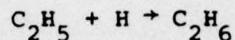
$$k_{ov} = A_{ov} e^{-E_{ov}/RT}$$

for disappearance of the primary fuel, (RH, for paraffins other than methane). Recent work has established that there are three stages in the paraffin oxidation process that must be considered if there is to be global modeling. The new element discovered is that there is a well-defined initial step very much like a pyrolysis sequence. This step is the relatively isoenergetic conversion of the paraffin to the olefin.

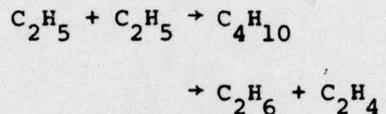
In addition studies of ethane pyrolysis have been completed. Results suggest that at flow reactor temperatures, the major termination step of the

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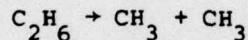
kinetic mechanism is



rather than



as suggested by other investigators. Preliminary determinations of the rate constant for



have been obtained and are in good agreement with values available from other studies.

Previous work in metal combustion led to an exploratory study of a number of chemiluminescent metal flames with the prospect of achieving population inversions between electronic states through chemical pumping. Experiments performed to find the most desirable constituents for a chemical laser device which would operate in the visible, near ultraviolet or near infrared region of the spectrum, have not been successful, but have provided much spectroscopic information about metal vapor-oxidizer systems.

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## I. Program Objective

### Abstract of Overall Research Effort

The AFOSR research efforts at Princeton have been concerned with the details of both rocket and air breathing combustion processes. The emphasis has been directed toward how fundamental physical, chemical, and aerodynamic approaches provide insight to these details. Fundamental approaches are presently oriented to give basic knowledge about the chemical kinetic aspects of propellant and jet fuel systems, the relationship of kinetics to the overall combustion process, plume formation resulting from the combustion, propellant sensitivity, pollutant formation, etc. In particular, the research has concentrated on the chemical kinetic processes occurring in the combustion of hydrocarbon fuels.

In addition, studies of metal vapor flames have been undertaken. A number of chemiluminescent metal vapor flames have been studied with the prospect of achieving population inversion between electronic states through chemical pumping.

### Objectives

The specific objectives of the research program have been to gain better insights in hydrocarbon pyrolysis in the presence of various oxygen concentrations. The application of semi-global model techniques to the problem has been a major objective of the program. In the metal vapor flame work, chemical reactions involving metal vapors offer an energetically promising avenue for the production of electronic level population inversions which could lead to lasing. Work under this program has considered several reaction systems with the objective of demonstrating the occurrence of population inversions which could potentially be used to develop high power lasers.

## II. Program Approach, Status, and Results

### Combustion Kinetics of Hydrocarbons

Interest in improving performance and the general emission characteristics of propulsive systems has created a need for developing a better understanding of the coupled fluid mechanical and chemical kinetic processes which occur in these devices. Modeling of the necessary combustion chemistry in systems using hydrocarbon fuels is impeded by the lack of adequate knowledge as to the detailed kinetic mechanism or the values of the absolute rate constants for many of the elementary reactions which are involved. It has been the intent of this research to develop a detailed description of these oxidation mechanisms through experimental measurements in a turbulent flow reactor developed earlier in this AFOSR program. Formulations of overall energy release and reactant consumption (product formation) expressions are developed as practical alternatives to the complete elementary kinetic mechanism. With these and other data, including detailed measurement of stable reactant, intermediate and product species taking part in the oxidation, a better understanding of the complete kinetic mechanism has evolved, and as has been shown in some cases, elementary rate constants for specific reactions can be measured.

Not only have the results of the current year followed along the lines proposed, but they have put the whole modeling question and overall hydrocarbon oxidation process in a better perspective while giving specific reaction rate data. Since the unique new interpretations could have only come about from the type of results obtained from the Princeton turbulent flow reactor, this device will again be reviewed. The next four subsections review some of the major results of the program and the current contract year in the broad context mentioned.

#### A. The Turbulent Flow Reactor

Basically, the Princeton flow reactor technique utilizes a heated cylindrical Quartz duct 10 cm in diameter through which a hot inert carrier gas flows at velocities which yield Reynolds numbers in excess of 3500 (Figure 1). The reactor assembly is constructed so that the reactor walls rapidly equilibrate to the local gas temperature. Rapid mixing of small amounts of pre-vaporized reactants with the carrier is provided by radial injection at the throat of a high velocity mixing inlet nozzle. Proper

adjustment of carrier temperature, flow velocity and reactant concentrations result in a steady, one-dimensional, adiabatic reaction zone extending over a length of approximately 85 cm. Simultaneous thermal and chemical data at discrete longitudinal locations in the reaction zone are obtained by longitudinal extension of an instrumented probe. Temperature measurements are made with a silica coated Pt/Pt-Rh thermocouple, and gas samples are removed through a water-cooled/expansion quenched stainless steel sampling probe. Consistent with the long range objective of more complex hydrocarbon oxidation studies, a sophisticated gas chromatographic chemical analysis procedure which was developed in the program (69), permits measurements of all stable hydrocarbon species (including partially oxidized compounds) as well as H<sub>2</sub> and O<sub>2</sub> to 1% precision.

Several unique advantages of this approach should be emphasized. By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, gradients are such that diffusion may be neglected relative to convective effects; thus the measured specie profiles are a direct result of chemical kinetics only. This is in contrast to low pressure one-dimensional burner studies where diffusion effects must be determined analytically before useful chemical kinetic data are obtained. While this procedure has progressed significantly in its refinement, estimation of diffusive corrections remain very difficult.

Furthermore, in the flow reactor uniform turbulence results not only in rapid mixing of the initial reactants, but radically one-dimensional flow characteristics. Thus "real" time is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well-defined since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that initial mixing history might therefore alter reaction phenomenon occurring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permit rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are functionally related to the local

mean flow properties. This conclusion is experimentally supported by excellent agreement of the derived chemical kinetic data with that obtained from shock tubes and static reactor systems at other temperatures. Agreement also substantiates that the reactor surfaces do not significantly affect the gas phase kinetics. Comparison of flow reactor data from reactor tubes of significantly different surface to volume ratio also corroborates this conclusion. Finally, and most important, the turbulent flow reactor approach permits kinetics measurements in a temperature range (800-1400 K) generally inaccessible to low temperature methods (fast flow Electron Spin Resonance, Kinetic Spectroscopy techniques, static reactors, etc.) and high temperature techniques (shock tubes, low pressure post flame experiments).

Many of the experimental studies were carried out in a newly designed, arc plasma heated turbulent flow system reactor (Figures 2 and 3) which has been completed and constructed entirely at University expense in the Engineering Quadrangle on the main University campus. In contrast to the flow reactor system described earlier in which packed bed heat exchangers serve as the hot gas generator \* [see Dryer (66) for detailed hardware description], the arc plasma concept permits precise control of flows characteristics up to twice the presently available mass flow and total enthalpy while eliminating carrier contaminants (carbon dioxide, water vapor). A direct liquid gas conversion system is the source of nitrogen carrier gas. Possible contaminants from anode/cathode erosion in the plasma jet have been controlled through a composite material design derived during the custom construction of the jet (TAFA division of Humphrey's Corp., Bow, N. H.). Ions are eliminated in a recombination/mixing plenum far upstream of the reactor. Available instantaneous heating characteristics accommodate rapid run preparation (the packed heat exchanger system requires approximately 8 hours preparation time) and maximum system temperatures to greater than 1500 K (the limit is imposed by reactor assembly materials). A ceramically filled, resistance heated inlet section mounted between the arc plasma generator and the reactor assembly has been designed to independently accommodate addition of up to two (thermally stable) reactant species as well as pre-vaporized water. This section is also necessary to produce uniform turbulent flow prior to the reactor assembly. Inlet

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\* This system on the Forrestal campus is to remain available for some concurrent use.

temperature to the assembly are monitored in this section with thermocouple instrumentation.

The reactor assembly itself is designed similar to the schematic of Figure 1. The main reactor tube is of fused silica ten centimeters in diameter and approximately 185 cm in length including a 28 cm nozzle inlet mixing section. Fused-silica walls further assure elimination of surface reaction effects. There are two additional reactor tube inserts available to reduce the test section diameter to 7.0 and 5.0 cm. Thus the reactor residence time range can be significantly shortened (factor of 4) and reactor surface-to-volume ratio increased (factor of 2). The reactor mixing inlet can accommodate independently controlled addition of up to 3 reactant species, including a pre-vaporized liquid. This feature is particularly important to some of the new work proposed in this document.

Gas samples are withdrawn through a water-cooled, convective quenched stainless steel probe with quenching gradient of greater than  $5 \times 10^6$  °K/sec. A Quartz coated Platinum, Platinum-Rhodium thermocouple with water-cooled jacket is used to measure the longitudinal reactor temperature distribution. Sampling instrumentation is extended longitudinally through the reactor section along its center line.

Gas samples withdrawn at up to twenty discrete longitudinal positions in the reactor are currently stored at low pressure in an all glass/teflon sampling assembly. Stable species including CO, CO<sub>2</sub>, aldehydes, alkanes, and other carbon containing species are measured using Hewlett-Packard 7624 Gas Chromatograph System equipped with electronic integrators and modified catalyst Flame Ionization detectors [Colket *et al.* (72)]. This approach permits identical sensitivity per gram atom of carbon for all carbon containing species (+1% Precision). Hydrogen, oxygen and nitrogen compounds are determined by thermal conductivity (+3% Precision).

#### B. General Modeling Considerations

Let us first consider the general oxidation characteristics of the normal alkanes. We shall exclude discussion of methane oxidation because it has received considerable attention in terms of detailed modeling [Westbrook *et al.*, J. Phys. Chem. (1977), Olson *et al.*, ACS National Meeting (1977)] and because its oxidation is dominated by (the difficulty of) methyl radical oxidation. This trait is not characteristic of any of the higher alkane oxidation systems and is the reason methane should not be used in experimental programs to represent a general hydrocarbon oxidation process. In these

discussions, it should be kept in mind that any empirical model must be quantitatively valid over a variety of fuel/air ratios and relatively wide ranges of pressure, temperature and residence times if it is to be useful in practical combustion modeling. Some recent experimental work at Princeton (77) adequately demonstrates many of the qualitative features of the hydrocarbon oxidation process and will be used later to quantitatively assess empirical modeling formulations.

By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, concentration gradients in this reactor are such that diffusion is negligible relative to the convective component; thus, the measured specie profiles are a direct result of chemical reaction alone. This fact has recently been corroborated in the modeling of methane/oxygen and moist carbon monoxide/oxygen experiments.

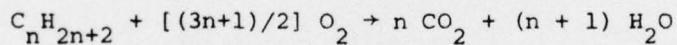
It is important to reemphasize that in this flow reactor, uniform turbulence results not only in rapid mixing of the initial reactants, but also in radically uniform, one-dimensional flow characteristics. Thus, real "time" is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well defined since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that the initial mixing history could therefore alter reaction phenomena occurring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permits rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are closely predicted by local mean flow properties (24). This conclusion is also verified experimentally by excellent agreement of the derived elementary chemical kinetic data with that obtained from shock tubes and static reactor systems at other temperatures [Colket *et al.*, Int. J. Chem. Kinet. 7, 223 (1975)] as well as by the initial analytical modeling efforts. These calculations also substantiate that the reactor surfaces do not significantly affect the gas phase kinetics of the large reactor core where measurements are made.

Figures 4 through 7 present data from the flow reactor for very fuel-lean oxidation of several alkane hydrocarbons above methane. The observed reaction profiles correspond to the "post-induction" phase of the oxidation. The

induction period, i.e., the reaction period dominated by initial thermal or chemical attack on a CH bond of the fuel and other secondary chemical kinetic initiation processes typically occurs in the mixing region of the flow reactor and is extremely short. (There are some exceptions to this general statement which will be discussed later.) The induction phase of the chemical kinetics process can be significantly modified or even eliminated in practical systems by backmixing or diffusion of partially oxidized species and radicals produced in the post induction zone and thus initiation chemistry is generally not of great importance in most combustion systems.

Figures 4-7 clearly show that even in very lean oxidation there appears to be an initial isoenergetic region in which the decomposition of the alkane takes place. The conversion of the alkane appears to be primarily to alkenes and is clearly an endothermic process. However, the hydrogen formed during this pseudo-pyrolysis step simultaneously reacts to form water. This reaction essentially compensates the endothermicity of the initial "pyrolysis" step.

Subsequently, and with some energy release, the unsaturated hydrocarbons are converted to carbon monoxide and hydrogen while the hydrogen present and being formed continues to oxidize. Finally, the large amount of carbon monoxide formed is oxidized to carbon dioxide, and most of the heat of reaction of the overall step



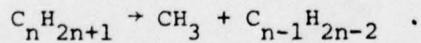
is released during this final reaction segment.

Earlier experimental investigations substantiate these qualitative observations for temperatures above 1000 K. As early as 1963, Orr presented shock tube results at 1 atm for n-heptane and iso-octane, and suggested similar behavior for these higher chain hydrocarbons. Levinson [Comb. & Flame 9, 63 (1959)] later repeated, confirmed and extended these earlier studies on n-heptane. Initial decomposition of alkanes through olefin formation in shock tube studies of "ignition delay" has also been noted by several other authors [Burcat et al., Thirteenth Int. Sym. on Comb. 745 (1971); Comb. Flame 18, 115 (1972); Cooke et al., Comb. Flame 24, 245 (1975)]. It should be noted that the induction period as defined earlier and ignition delay measurements only correspond closely for methane. For the higher hydrocarbons, shock tube ignition delay (especially when determined by pressure rise) corresponds more closely to the characteristic time required for carbon

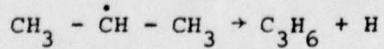
monoxide oxidation to begin. Major reaction of the initial fuel (and even the olefins formed) should logically occur more to the oxidation of carbon monoxide since the reaction rates constants of the reactions are one to two orders of magnitude faster than that for carbon monoxide [Walker, SPR Chem. Soc., Reaction Kinet. 1, 161 (1975)]. The shock tube observations of Hawthorne and Nixon [AIAA J. 4, 513 (1966)] qualitatively confirm these arguments by the fact that ignition delay for propane and its decomposition products (mixtures of propene and hydrogen) were found to be very similar.

It is well known that if a tertiary carbon exists in a hydrocarbon the hydrogen attached to it will be abstracted first, and if no tertiary-carbon atom is available, a hydrogen atom will be abstracted from the secondary carbon in the chain. There is no doubt that the initial attack on alkanes is a hydrogen abstraction by OH, H, and O radicals, and in fact, the elementary rate data taken from the previously cited work of Walker show that the position of attack is a question of relative rates. Multiple tertiary carbon atoms are normally not encountered in a given hydrocarbon compound whereas one must realize that there are at least six CH bonds on terminal carbon atoms in every alkane structure. Thus, for example, if the difference in bond energy and the number of various bonds available, is taken into account at 1000 K, radicals formed from attack on a secondary compared to an primary carbon for propane and n-butane will be approximately 1 and 2.

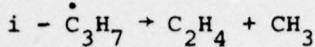
In their review Fristrom and Westenberg (Flame Structure, McGraw Hill, 1965) state that the hydrocarbon radicals thus formed decompose into a methyl radical and an olefin with one less carbon number



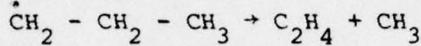
However, this general statement is not supported by flow reactor data for oxidation of the hexane isomers as shown in Figures 8 and 9. There should be a great preponderance of pentenes compared to other olefins early in the reaction if Fristrom and Westenberg's general statement were correct. However, experiments on deuterated compounds show that when a radical decomposes, a bond once removed from the site is broken -- since in this case both a proton and hydrogen atom shift are not required. In addition, when there is a choice between a CH bond and a CC bond in these radicals, the CC bond is usually broken due to the lower bond strength. Thus, one finds



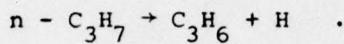
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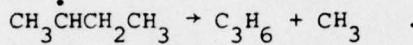
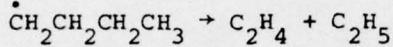
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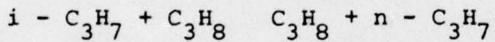
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In the case of butyl radicals one finds:



There has been some unresolved controversy over whether any decomposition through the unfavored routes can occur. Some investigators have claimed that no direct decomposition via these reactions can take place, but that an internal rearrangement must occur before decomposition can occur by an unfavored route. Others claim that reactions such as

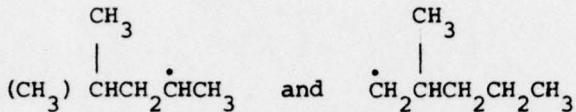


are fast and lead to the alternate routes. However, experiments (McNesby et al.. J. Chem. Phys. 24, 1260 (1956); J. Amer. Chem. Soc. 83, 4891 (1961); J. Chem. Phys. 36, 2272 (1962); J. Chem. Phys. 37, 1610 (1962)] show that though these alternate modes might occur, they are negligible below 800 K, but could make some contribution above 900 K.

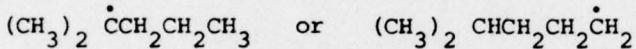
The results presented in Figures 8 and 9 tend to confirm the one bond removed rule and indicate that there is little or no decomposition by unfavored paths. In the case of propane, the rate constants for hydrogen abstraction indicate that iso- and normal-propyl radicals should be formed in nearly equal amounts, and therefore, one should find equal amounts of ethene and propene. In fact, one finds that the ethene formed is 1.5 times the propene. This result could lead one to argue for isomerization reactions, but it is more likely that the extrapolation of the rate constants of radical attack on the primary fuel leads to the discrepancy. For butane, one predicts twice as much sec-butyl as n-butyl, but each n-butyl decomposes to an ethene and an ethyl radical and the ethyl will usually decompose to another ethene. Thus,

again one expects nearly equal amounts of ethene and propene and again one finds 50% more ethene than propene.

The real confirmation of the rule come from the isohexane experiments presented in Figures 8 and 9. In the 2-methylpentane experiments the favored radicals are

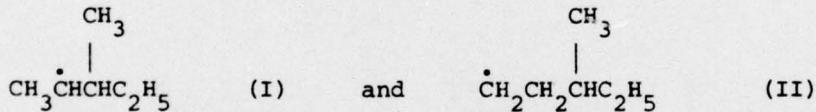


The former radical decomposes to  $\text{C}_3\text{H}_6 + i - \text{C}_3\text{H}_7$  and therefore ultimately to two propenes while the latter form  $\text{C}_3\text{H}_6 + n - \text{C}_3\text{H}_7$  (or 1-pentene +  $\text{CH}_3$ ). Thus,  $\text{C}_3\text{H}_6$  should greatly dominate  $\text{C}_2\text{H}_4$ , which is explicitly what is observed experimentally. Furthermore, only isobutene will form from



Since only one butene is observed, this result also seems to fit well with the one bond removed concept.

3-methylpentane, on the other hand, will react mainly to the radicals



The first decomposes to  $2 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_5$  (ultimately  $2 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_4$ ) and the second forms  $\text{C}_2\text{H}_4 + \text{sec} - \text{C}_4\text{H}_9$  (ultimately  $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ ). Of the other radicals



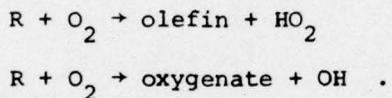
decomposes to  $1 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_5$ , while



forms a pentene (2-methyl-1-butene) and a methyl radical. These predictions are also consistent with the observed results, in which  $[\text{C}_2\text{H}_4] > [\text{C}_3\text{H}_6]$ . The ethene is larger than butene because of the decomposition of radical (II) and because butene reacts faster than ethene. Furthermore, three butenes are observed: 1-butene, cis-2-butene, and trans-2-butene.

All these results appear to confirm the "one bond away from the radical site" theory of decomposition. Furthermore, the finding of only one butene product in the 2-methylpentane oxidation indicates that the isobutyl radical does not isomerize or break down in a non-standard fashion at 1000 K, unless it is in very small amounts. Thus, by estimating the probability of hydrogen abstraction based on the number of hydrogens available on each carbon atom, ease of removal in each case, and considering the cleavage rule discussed above, the concentration trends of olefin and lower alkanes derived from Figures 4-9 are quite predictable. These data are presented in Table I.

In addition to the decomposition reactions already discussed, the more complex radicals can also react directly with oxygen



It is important to note here that the competitive rates of the first of the above reactions and the ethyl radical decomposition reaction may be particularly critical in describing oxidation of ethane and perhaps that of the higher order alkanes. As pointed out by Walker, the latter of the above two reactions probably occurs in two or more steps. At temperatures below 800 K, the nature of the oxygenate depends on which radical is attacked. Many other routes are also available for formation of oxygenated species.

Figures 10 and 11 present results for the oxidation of ethane at equivalence ratios near one and one and one half.

Although on these more fuel rich studies, the same overall qualitative features of the oxidation reaction hold, the relative concentrations of intermediate species vary. The comparative characteristic times of alkane and alkene conversions are different (both from concentration and temperature effects) and the CO oxidation becomes almost non-existent as the oxygen concentration is lowered. In these richer systems hydrogen is no longer oxidized at a rapid rate to water and itself becomes an important intermediate species. Finally, it is worth noting the appearances of acetylene as an intermediate oxidation species under rich conditions. The point (time) of appearance indicates that it is an intermediate in the oxidation of the olefin, possibly produced by vinyl radical decomposition [Jachinowski, Comb. Flame 29, 55 (1977)]. Since the production of soot precursor species is most likely related to the polymerization of acetylenic intermediates, the relation of

acetylene production and oxidation to the olefin oxidation will be of value to understanding soot formation.

Summarizing the general characteristics of high temperature alkane oxidation:

- 1) As a result of the relatively difficult oxidation of methyl radicals, methane exhibits a very long induction period and its oxidation is not characteristic of the higher paraffins.
- 2) The induction for higher hydrocarbons is very short relative to the total fuel lifetime and can be neglected under most practical combustion modeling situations.
- 3) The oxidation of the higher paraffins qualitatively proceeds through three distinct but overlapping phases.

- a. conversion of the alkanes to alkenes with the available hydrogen simultaneously converted to water
- b. conversion of the alkenes formed to carbon monoxide with the available hydrogen simultaneously converted to water
- c. conversion of carbon monoxide to carbon dioxide.

The simultaneous conversion of hydrogen is dependent on the amount of oxygen available and is potentially modified by the presence of hydrocarbons. Almost all of the energy release occurs from the conversion of carbon monoxide to carbon dioxide.

4) The relative quantities of olefins produced can be qualitatively estimated by considering site reactivity, the number of hydrogen abstraction sites and a "one bond away from the radical site" rule for decomposition.

5) In fuel-rich alkyl oxidation systems, acetylene will form probably as a result of olefin oxidation and may be linked to the production of soot precursor species.

The above qualitative characteristics appear to apply over a relatively wide temperature range, at least for the case of ethane (77), and provide a reasonable behavioral model to which empirical formulations should be compared.

#### C. Empirical Modeling Concepts

The larger number and poor definition of the elementary reaction mechanisms necessary to detail the chemistry and the lack of evaluated rate constants for many of the included elementary steps has led both the fundamental kineticist and those who model to conclude that detailed approaches are presently intractable for realistic fuels. Yet, it is well recognized

that detailed modeling may be required to properly account for the significant coupling of hydrocarbon, carbon monoxide, and NO<sub>x</sub> kinetics, particularly in fuel-rich combustion. Thus far, only approximations of detailed chemistry have been employed to estimate rate of energy production and/or production of partially oxidized species from higher paraffin fuels. These schemes are in the form of "global" or "quasi-global" kinetic mechanisms.

The concept of overall (global) reaction kinetics and its use is a direct result of the complexity of most chemical reactions and the complicated fluid mechanical situation in which some knowledge of heat release and chemical rates is necessary (74). The assumption invoked is that the course of chemical kinetic events may be described in terms of a few of the principal reactants and products (C<sub>i</sub>) in a functional relation with much the same form as an elementary reaction process. Typically, the equation is of the form:



The rate for this process is defined by

$$-\frac{d[C_1]}{dt} = k_{ov} \sum_{i=1}^m [C_i]^{n_i} \quad II$$

k<sub>ov</sub>, the overall specific rate constant, is expressed in the Arrhenius form where

$$k_{ov} = f(T)A e^{-E/RT}$$

The n<sub>i</sub>'s are defined as the orders of reaction with respect to C<sub>i</sub> but are not necessarily equal to the stoichiometric coefficients of the overall reaction. Σ<sub>i</sub> is termed the overall reaction order. The product of f(T) and A is termed the overall frequency factor and, E is referred to as the overall activation energy.

These relations imply nothing about the actual kinetic mechanism (in terms of elementary reactions), although the parameters in the strictly empirical rate relation are sometimes governed by a single elementary step (or a number of steps) which basically controls the rate of the chemical process. Under what circumstances such an overall correlation is usable is largely dependent on both the detailed kinetic behavior of the reaction and the physical environment in which the expression is derived. For example, Levy and Weinberg [Comb. Flame 3, 229 (1959)] concluded that such an approach

is not generally applicable to chemical measurements taken in flames; this fact may not arise from the chemistry itself, but from the physical structure and diffusive character of the flame studies.

Where a particular rate-determining step or sequence in the true chemical reaction mechanism occurs and the physical circumstances of the application are similar to those from which the expression was derived, the overall approximation is a valid and vastly simplifying idea. However, extension of such a correlation to experimental conditions outside the range of parameters for which it is derived should never be performed without experimental and/or analytical verification and only then with some reservation. Unfortunately, there is currently little hope of avoiding this problem in the case of modeling hydrocarbon combustion.

Single step global reaction schemes commonly have been used in many combustion modeling exercises. Yet the only actual oxidation reactions for which parameters have been derived experimentally are those of methane and moist carbon monoxide.

Considerable global modeling studies have been performed on carbon monoxide and these have been reviewed by Dryer (66) and Howard *et al.* [Fourteenth Comb. Symp. 975 (1973)]. Methane ignition and oxidation kinetics have also been expressed in this manner, often in conjunction with developing detailed mechanisms, and many of these studies have also been reviewed (66).

The post induction reaction of methane-oxygen mixtures was studied by Dryer and Glassman (66,67) and their results lent encouragement to the belief that the rate of hydrocarbon consumption could be expressed by a simple global expression of the form of Equation II.

The rate of reaction in the post induction phase of the lean methane oxidation experimentally was found to be described well by the overall expression

$$-\frac{d[\text{CH}_4]}{dt} = 10^{13.2 \pm 0.2} e^{-(48400 \pm 1200)/RT} [\text{CH}_4]^{0.7} [\text{O}_2]^{0.8}$$

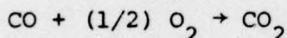
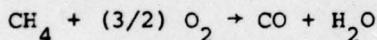
It should be noted that the parameters of this equation are significantly different than those found by investigators who have studied the induction (ignition delay) phase of this reaction in shock tubes and flow reactors. A review of available data through 1973 predicts the rate of reaction to be inhibited by the concentration of methane. Seery and Bowman [Comb. Flame 14, 37 (1970)] empirically correlated the ignition delay time as

$$(1/\text{Reaction Rate}) \sim \tau = 7.65 \times 10^{-18} e^{+51400/RT} [\text{CH}_4]^{0.4} [\text{O}_2]^{-1.6}$$

and developed a detailed elementary mechanism which reasonably predicted the relation. Figure 12 shows a comparison of the overall rate constant derived by Dryer (66) and the results calculated from parameters predicted by detailed analytical studies of Bowman [Comb. Sci. and Tech. 2, 161 (1970)]. The analytical overall rate constant was calculated from

$$k_{\text{ov}} = - (d[\text{CH}_4]/dt)/([\text{CH}_4]^{0.7} [\text{O}_2]^{0.8})$$

Clearly there are two phases of this reaction which are not modeled by the same global parameters. Indeed, the experimental flow reactor data of Dryer show similar behavior (Figure 13). As described earlier, it is the post-induction reaction which is most important to practical combustion, and it is evident from Figure 12 that the relation which gives the overall general disappearance readily predicts the same qualitative behavior as the detailed methane oxidation mechanism over a wider temperature range and equivalence ratio than the experiments from which it was derived. Dryer (66) completed the modeling of methane oxidation using a two step global representation:



with the reaction rates described by

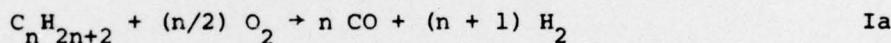
$$-d[\text{CH}_4]/dt = 10^{13.2 \pm 0.2} e^{-(48400 \pm 1200)/RT} [\text{CH}_4]^{0.7} [\text{O}_2]^{0.8}$$

$$+d[\text{CO}_2]/dt = 10^{14.6 \pm 0.25} e^{-(40000 \pm 1200)/RT} [\text{CO}] (\text{H}_2\text{O})^{0.5} [\text{O}_2]^{0.25}$$

It should be noted that both the overall rate constants and the reaction orders were experimentally derived, i.e., no parameters were assumed. Westbrook and Chang [Central States Meeting of The Comb. Inst., March 1977] have recently compared calculated flame propagation through premixed and stratified mixtures using both the detailed methane oxidation mechanism derived by Westbrook *et al.* [J. Phys. Chem. (1977)] and a global model for methane disappearance only (i.e., the overall heat of reaction was proportionally released with respect to methane disappearance). Results showed reasonable predictions could be globally achieved over a wide range of pressures and temperatures for propagation through premixed gases, but flame propagation

through stratified mixtures was not well simulated by the single step global model. Only Appleby *et al.* [J. Amer. Chem. Soc. 75, 1809 (1953)] have attempted global modeling of higher paraffin oxidation (butane); however, those studies correlated only the maximum reaction rate of the initial fuel, are outside the temperature range of present interest ( $T \approx 800$  K) and involved modeling only of the disappearance of the initial fuel. Global reaction modeling might have some potential for describing spatial energy release and reactant/final product distribution for higher hydrocarbons only if more than one global step is used.

Edelman and Fortune [AIAA Seventh Aerospace Sciences Meeting, #69-86 (1969)] have extended the multistep concept by developing a "quasi-global model" which combines the use of both global expressions and elementary reactions. Edelman and Fortune chose to approximate the higher paraffin oxidation to carbon monoxide and hydrogen as a unidirectional global reaction



with the rate given by

$$-\frac{d[C_n H_{2n+2}]}{dt} = [C_n H_{2n+2}]^a [O_2]^b k_{ov} \quad IIa$$

and combined these equations with a number of elementary reactions from the hydrogen/oxygen and carbon monoxide/oxygen reaction mechanisms.

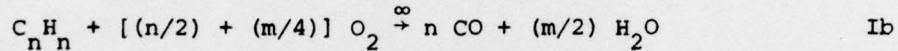
Values of  $a = 1/2$  and  $b = 1$  were assigned and

$$k_{ov} = 1.8 \times 10^9 w^{-0.5} [T/1111 - 0.5] T^{0.5} p^{-0.2} e^{-13740/RT}$$

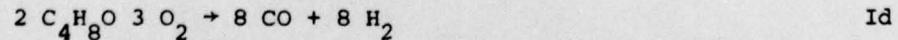
was initially determined from results of an analytical study of propane ignition kinetics.  $w$  is the average gram molecular weight of the reacting system, and dimensions in this equation are cal, K, moles-cm<sup>-3</sup>, atm, sec. Edelman and Fortune suggested 800 - 3000 K as the applicable temperature range. An attempt to validate the assumption that a quasi-global model based on propane characteristics also applied to higher paraffins was made by comparing the magnitudes of the ignition delay determined in the shock tube experiments of Nixon *et al.* [Shell Development Company Reports, Parts I-III (1967)]. These experiments identified some similarity in the functional behavior and the order of magnitude of the ignition delay times for propane and n-octane/oxygen mixtures. The quasi-global model using various global reaction rates and in some cases an extended set of CHO reactions has been employed extensively by its developers in combustion ignition and combustion-emission modeling, and

notable successes have been reviewed on several occasions. The variation in the overall rate constant expression used for paraffin oxidation was a result of accumulating new experimental data from which the rate constant was derived. While the variation at one atmosphere has been over a factor of 30 at times, the first and the most recently quoted values are very similar (within a factor of 4 over 1000 to 2000 K). However, the pressure dependence of the relations are different, and as pressure increases, the more recent expression will predict a slower reaction rate.

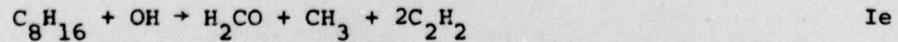
Modified mechanisms based on the quasi-global concept have also appeared in the literature. In attempting to predict gas turbine combustion NO<sub>x</sub> emissions, Mellor [Comb. Sci. and Tech. 6, 279 (1973)] has replaced Equation Ia with



and defined the rate constant of Equation IIa as infinite. This modification was based upon the results of Marteney [Comb. Sci. and Tech. 1, 461 (1970)]. However, Bowman in comments to Edelman et al. showed that "infinite" quasi-global kinetics do not offer any significant advantages over the partial equilibrium approach for prediction of NO<sub>x</sub> emissions. It should be noted that these calculations also show that quasi-global finite, and quasi-global infinite, kinetics are equally capable of estimating NO<sub>x</sub> emissions for residence times which are long in comparison to the time necessary to complete hydrocarbon combustion to its equilibrium product distribution. Thus, it should be remembered that in many cases and particularly for lean oxidation, prediction of NO<sub>x</sub> emissions may not be a sensitive enough test to judge the qualities of a proposed hydrocarbon oxidation model. Roberts et al. [AIAA J. 10, 820 (1972)] have also derived a combustion mechanism based upon the results of Edelman. Equation Ia was initially replaced with a set of two reactions



and finally modified to include a third reaction



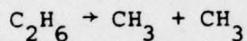
to describe the initial fuel disappearance. The model also significantly modified and extended the set of elementary reactions included by Edelman and Fortune and added a number of intermediates (non-elementary) reactions of

species such as HCO,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , etc. The mechanism derived in this manner has been used in numerical calculations for gas turbine combustors to predict the formation of nitric oxide, the effects of water addition on  $\text{NO}_x$  emissions, carbon monoxide production in the primary zone (including droplet effects), and emissions produced by methanol and jet fuels.

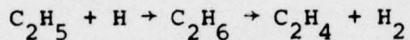
These efforts cannot be reviewed comprehensively here, but it is of importance to note that the initial publication on quasi-global modeling forms the conceptual and quantitative basis for the desired model.

#### D. Ethane Pyrolysis and Oxidation Studies

Ethane pyrolysis studies in the laboratory (73,77) have produced elementary data for the reaction



which is in good agreement with other workers. The reaction



has been shown to be important to chain termination in pyrolysis.

Studies of both lean and rich regions of the oxidation of ethane have been completed. It has been established that a correlation of the type

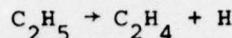
$$-\text{[C}_2\text{H}_6] \sim ([\text{C}_2\text{H}_6]_0 - [\text{C}_2\text{H}_6])^a$$

appears to give a good representation for the initial phase of the disappearance of ethane in its oxidation. More extensive work (77) has shown that this correlation only holds over part of the range of equivalence ratios studies. The completed work on ethane covered an equivalence ratio between 0.04 and 3.2 and an initial temperature range of 950 - 1150 K. Of course, all work was at atmosphere pressure.

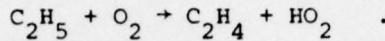
Ethane oxidation appears to follow two different patterns according to two equivalence ratio regimes. The first is a fuel-lean regime in which the limits are defined by a parameter  $0 \leq \alpha \leq 2.2$ . The other is called a fuel-rich regime and is defined by  $\alpha \geq 5$ . Obviously then there exists a regime  $2.2 \leq \alpha \leq 5$  for which both mechanisms affecting oxidation characteristics are comparable. The parameter  $\alpha$  is defined by

$$\alpha = k_p/k_{\text{ox}} [\text{O}_2]_0$$

where  $k_p$  is the rate constant for the pyrolysis step



and  $k_{\text{ox}}$  is the rate constant for the oxidation step



These results and the explanations to follow are given in great detail in Cohen's Ph.D. Thesis (77).

The fuel-lean regime is characterized by a long induction-like reaction region in which the ethane disappearance is given by

$$-\dot{[\text{C}_2\text{H}_6]} = 10^{14.38+0.28} e^{-(55250+2500)/RT} ([\text{C}_2\text{H}_6]_0 - [\text{C}_2\text{H}_6])^{0.8} [\text{C}_2\text{H}_6]^{0.4} [\text{O}_2]^{-0.1}$$

This region is then followed by one in which

$$-\dot{[\text{C}_2\text{H}_4]} = 10^{14.96+0.23} e^{-(63840+1120)/RT} [\text{C}_2\text{H}_4]^{1.05} [\text{O}_2]^{-0.1}$$

Intermediates observed in this regime were  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{C}_2\text{H}_4\text{O}$  with traces of propane, propene, acetylene, and formaldehyde.

In the stoichiometric and fuel-rich regime, the ethane reaction rate was found to correlate but as

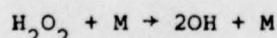
$$-\dot{[\text{C}_2\text{H}_6]} = 10^{13.41+0.45} e^{-(39210+2500)/RT} [\text{C}_2\text{H}_6]^{0.8} [\text{O}_2]^{0.75}$$

The ethane oxidation rate was determined to be

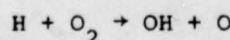
$$-\dot{[\text{C}_2\text{H}_4]} = 10^{11.92+0.37} e^{-(50970+1770)/RT} [\text{C}_2\text{H}_4]^{0.25} [\text{O}_2]^{0.85}$$

The same intermediates were found in this regime and were in larger quantities with the exceptions of  $\text{CH}_3\text{CHO}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CH}_2\text{O}$ .

The difference in the oxidation regimes has been shown (77) to be the result of a shift in the primary branching reaction from



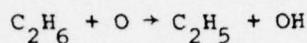
in the lean regime to



in the stoichiometric and rich regime. This result suggests that



is not the only reaction of importance destroying ethane, but that



must also be significant depending on the stoichiometry.

#### Metal Combustion Laser Work

Previous work in metal combustion led to an exploratory study of a number of chemiluminescent metal vapor flames with the prospect of achieving population inversion between electronic states through chemical pumping.

Of particular interest, the low pressure diffusion flames of Mg and Ca reacting with a mixture of  $\text{CCl}_4$  and  $\text{O}_2$  were found to give extensive metal atom line emission up to the ionization limit of each metal. Emissions were also observed from the metal monochloride and the high-pressure bands of  $\text{C}_2$ . A detailed examination of these flame systems (75) has revealed that, inasmuch as high levels of non-equilibrium excitation were observed among atomic states, the flames gave neither population inversions nor excited state populations high enough to sustain the losses in a typical laser cavity.

More recently, the emissions from metal vapor/ $\text{CCl}_4/\text{O}_2$  flames employing the alkali metals (Li, Na, and K) have been examined. These flames differed from those produced with Mg and Ca in that the metal atom excitation was much weaker and only the lowest atomic energy levels showed population. There was no metal halide emission, but the high-pressure bands of  $\text{C}_2$  were stronger. A study of the intensity distribution of atomic states showed no population inversions. An absolute measurement of the photon yield was not made, because comparisons with the Mg and Ca photometric readings indicated that the yields from the alkali metal/ $\text{CCl}_4/\text{O}_2$  systems were even less than those of the alkaline earth metal/ $\text{CCl}_4/\text{O}_2$  systems.

Other systems that appeared to have some possibility by virtue of their visibly strong chemiluminescence were the alkali metal/ $\text{POCl}_3$  flames that give polyatomic ( $\text{POCl}_2$ ) emission in the 4100A to 5000A region of the spectrum. Inverted Polanyi flames of Li, Na, and K reacting with  $\text{POCl}_3$  have all been found to give the same emission spectrum except for weak atomic excitation characteristics of the metal used.

Absolute intensity measurements showed imperceptibly low proton yields based on the  $\text{POCl}_3$  consumption rate. The Li/ $\text{POCl}_3$  flame gave the highest photon yield of  $10^{-4}$  photons/molecule. Those of K and Na flames were approximately  $2 \times 10^{-5}$  photons/molecule and  $2 \times 10^{-6}$  photons/molecule respectively.

There was no visible evidence of such effects as stimulated emission and self absorption. Note, the apparatus has a multiple reflection cavity (or White cell) that can be used to detect self absorption and stimulated emission.

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Table I

RELATIVE HYDROCARBON INTERMEDIATE CONCENTRATIONS PRODUCED  
DURING OXIDATION OF SEVERAL PURE ALKYL-HYDROCARBONS

<u>Fuel</u>	<u>Relative Hydrocarbon Intermediate Concentrations</u>
ethane	ethene >> methane
propane	ethene > propene >> methane > ethane
butane	ethene > propene >> methane > ethane
hexane	ethene > propene > butene > methane >> pentene > ethane
2-methyl pentane	propene > ethene > butene > methane >> pentene > ethane
3-methyl pentane	ethane > butane > propane > methane >> pentene > ethane

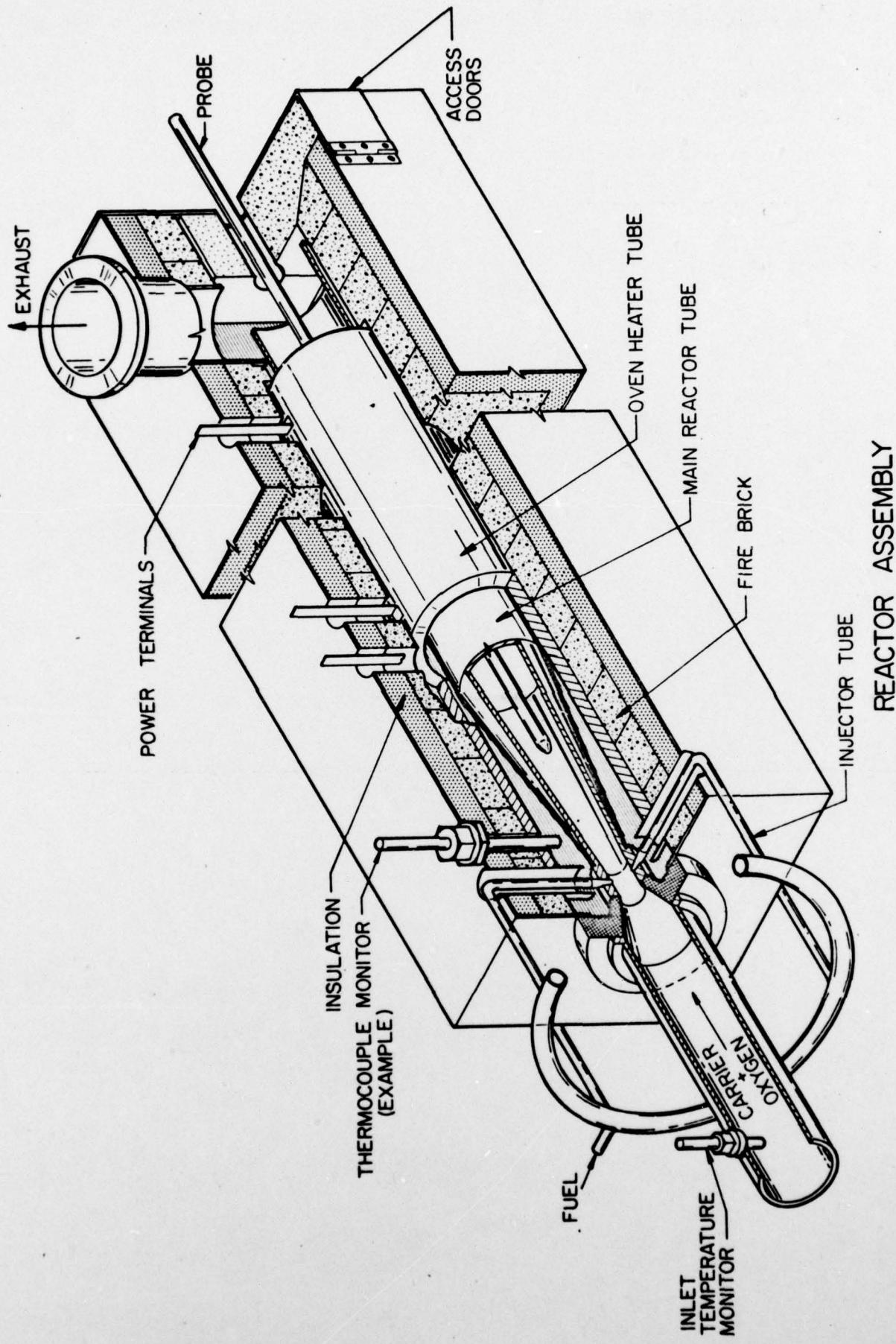
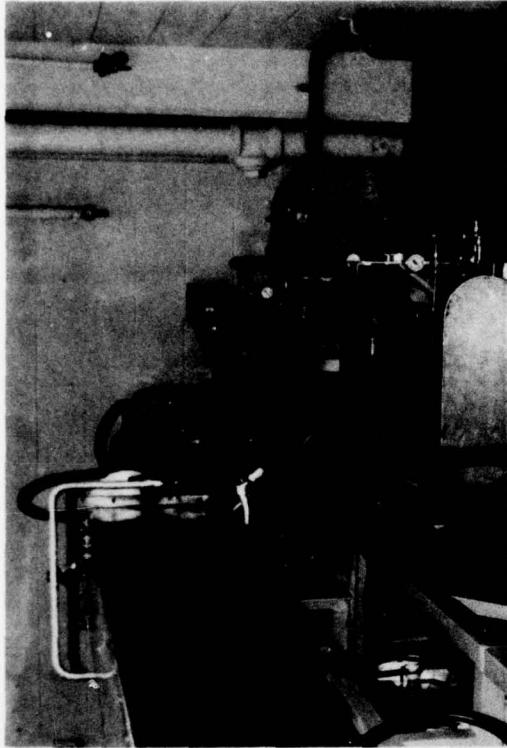


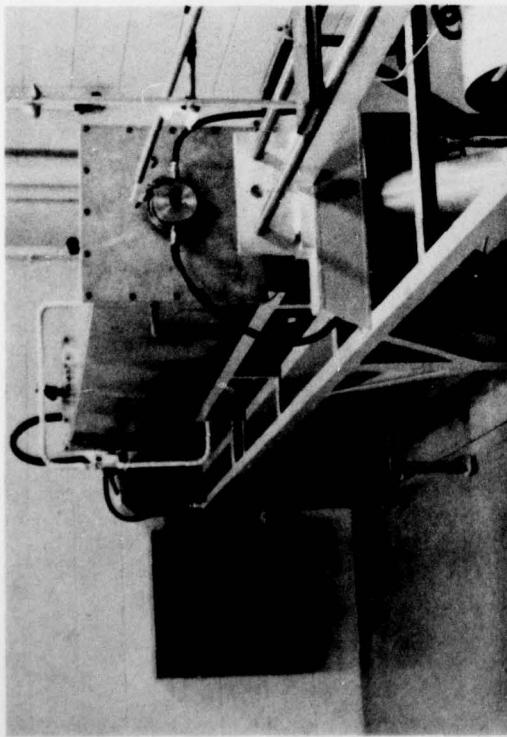
FIGURE I



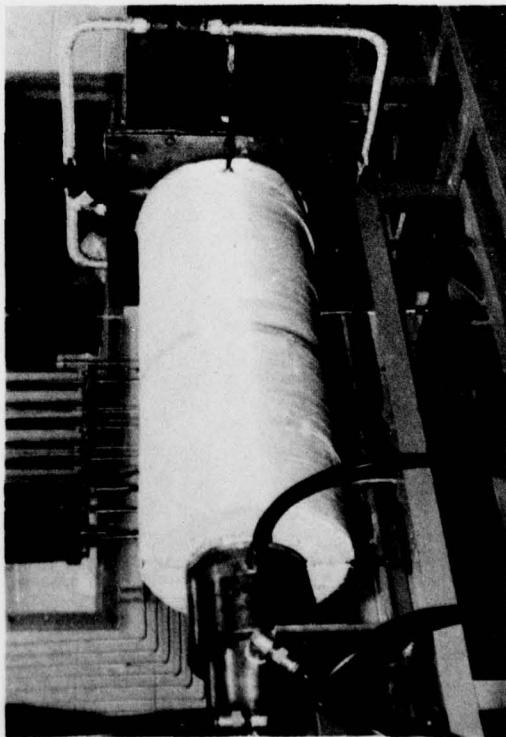
REACTOR ASSEMBLY AND COOLING SYSTEM



SAMPLING PROBE

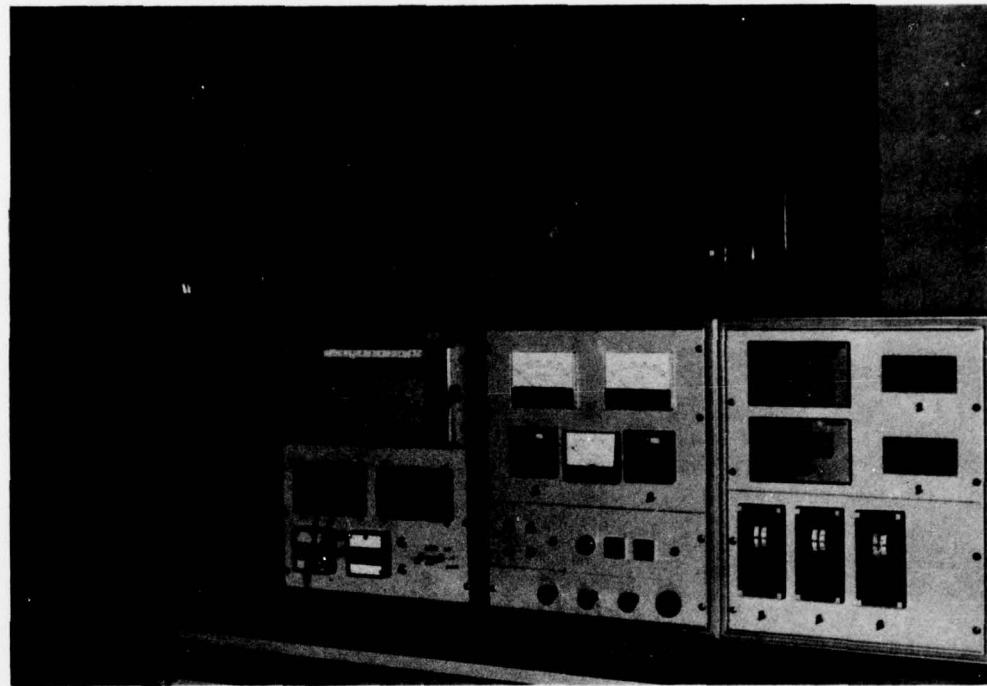


REACTOR ASSEMBLY

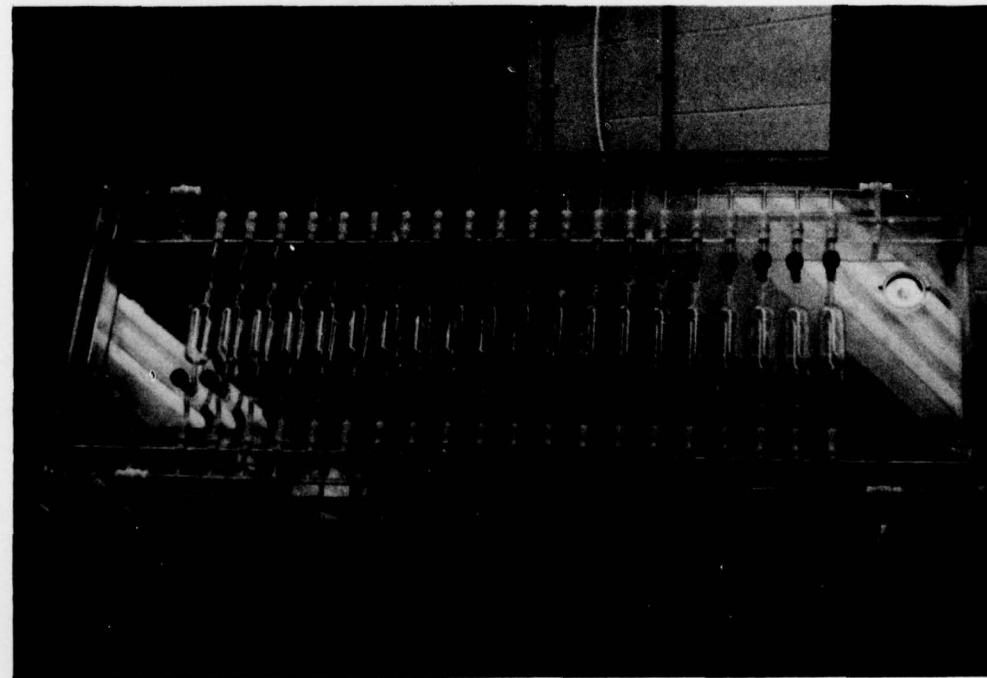


INLET SECTION AND PLASMA TORCH

FIGURE 2

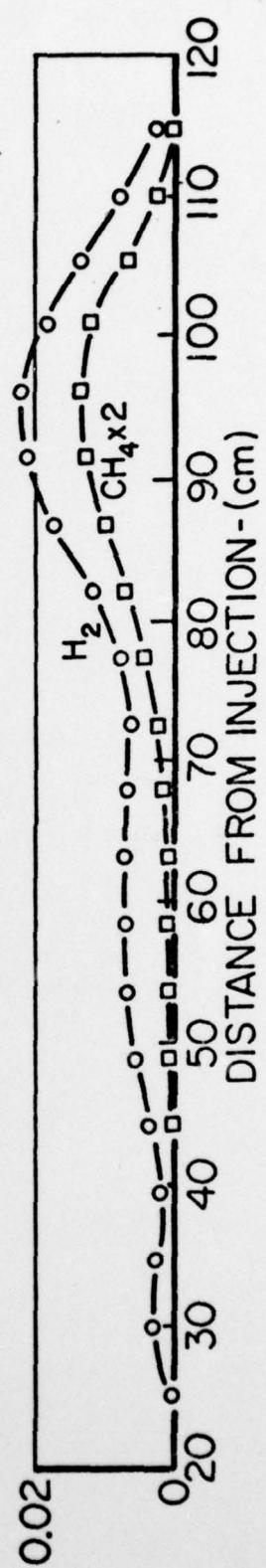
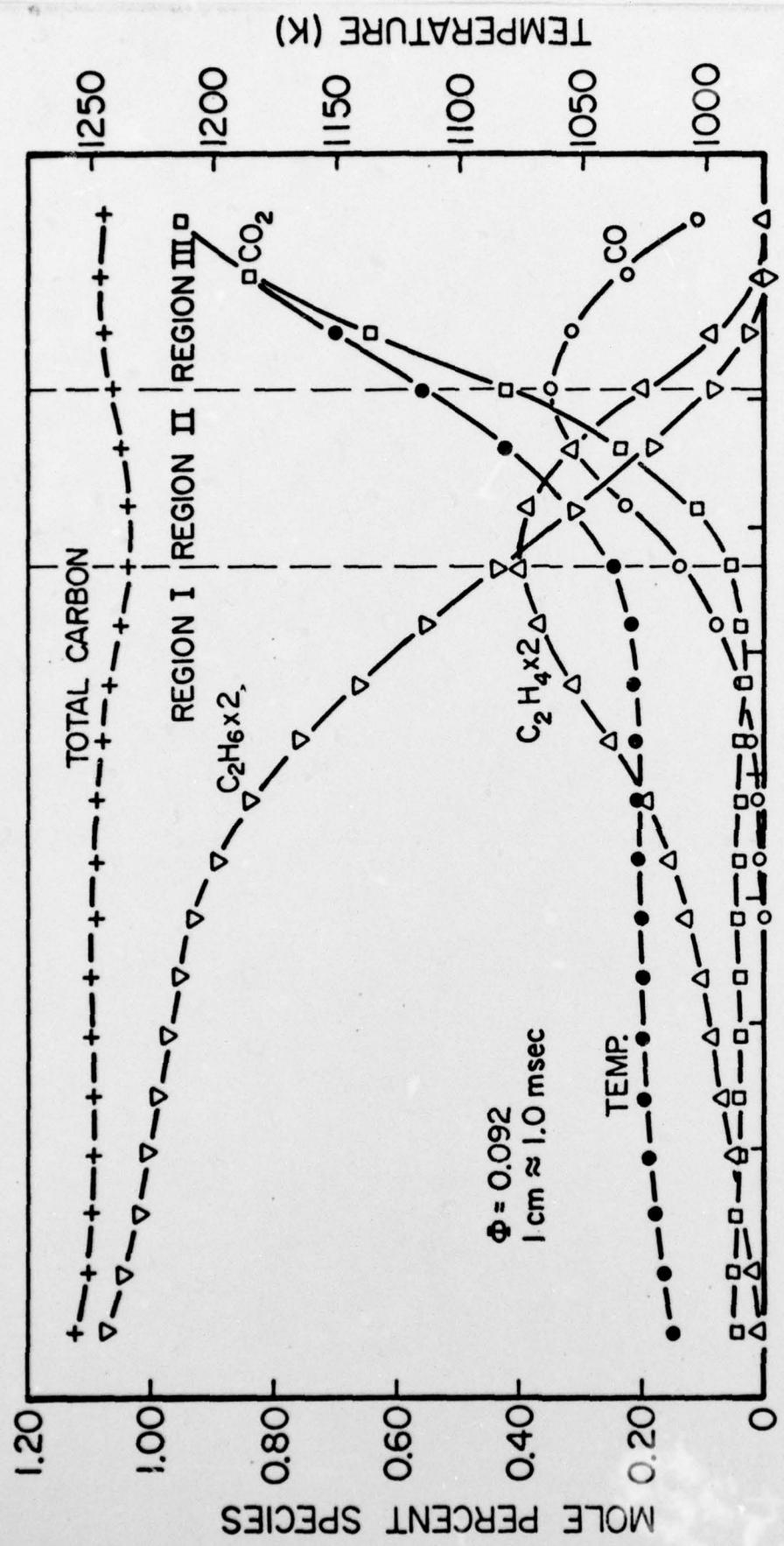


FLOW REACTOR CONTROL PANEL



SAMPLING RACK

FIGURE 3



CHEMICAL COMPOSITION OF SPREAD ETHANE - AIR REACTION

FIGURE 4

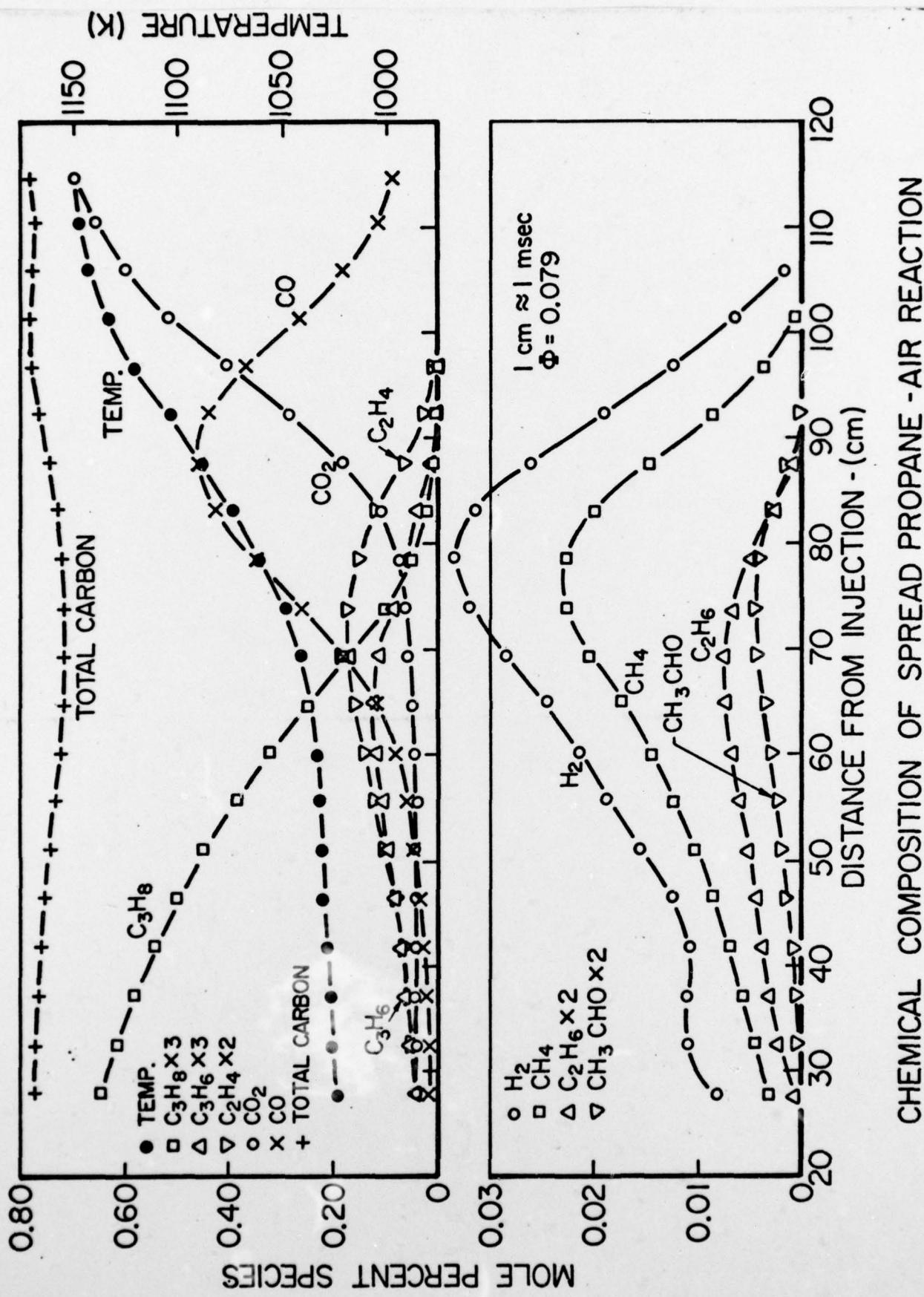


FIGURE 5

CHEMICAL COMPOSITION OF SPREAD PROPANE-AIR REACTION

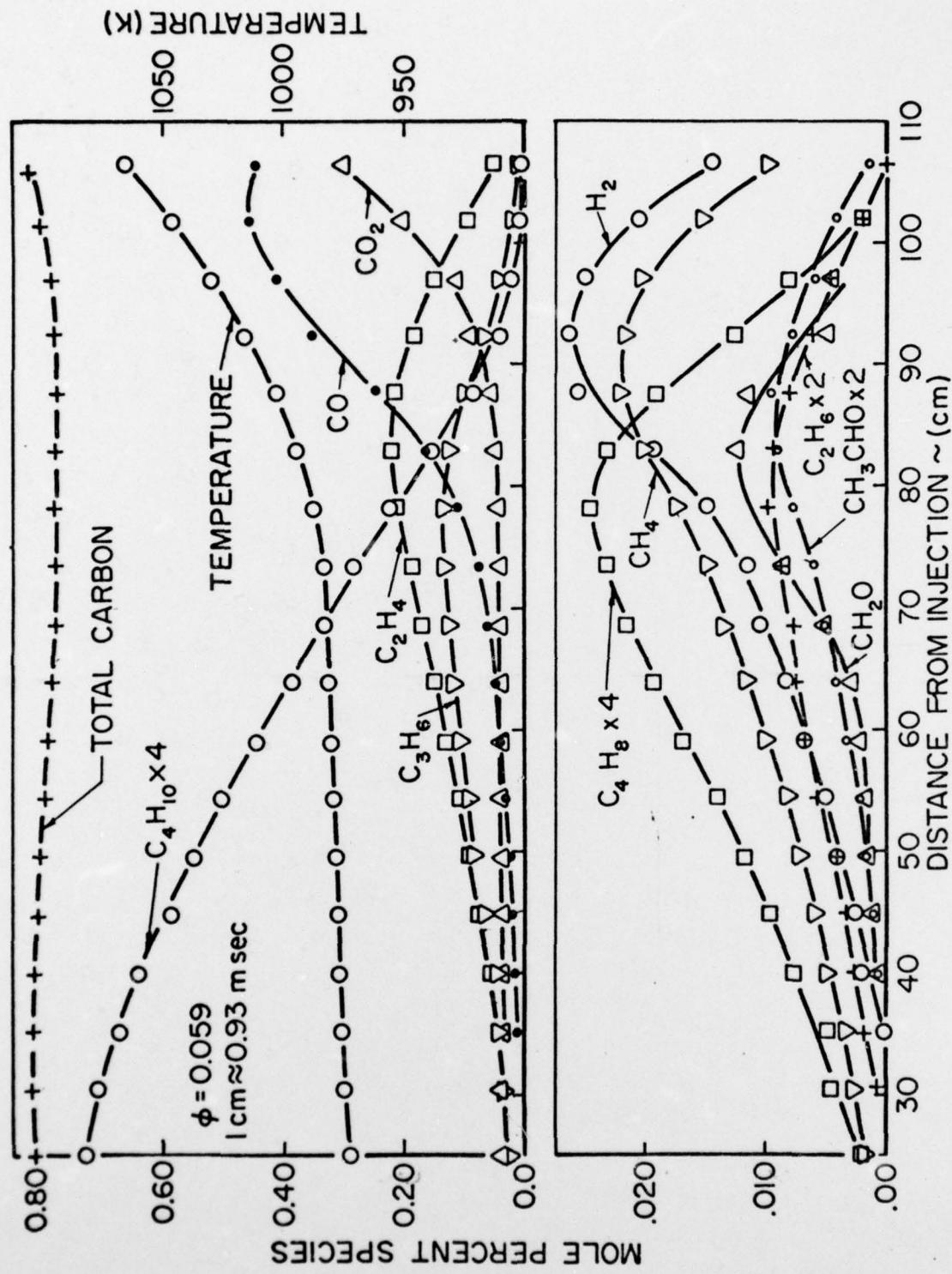


FIGURE 6

CHEMICAL COMPOSITION OF SPREAD n-BUTANE-AIR REACTION

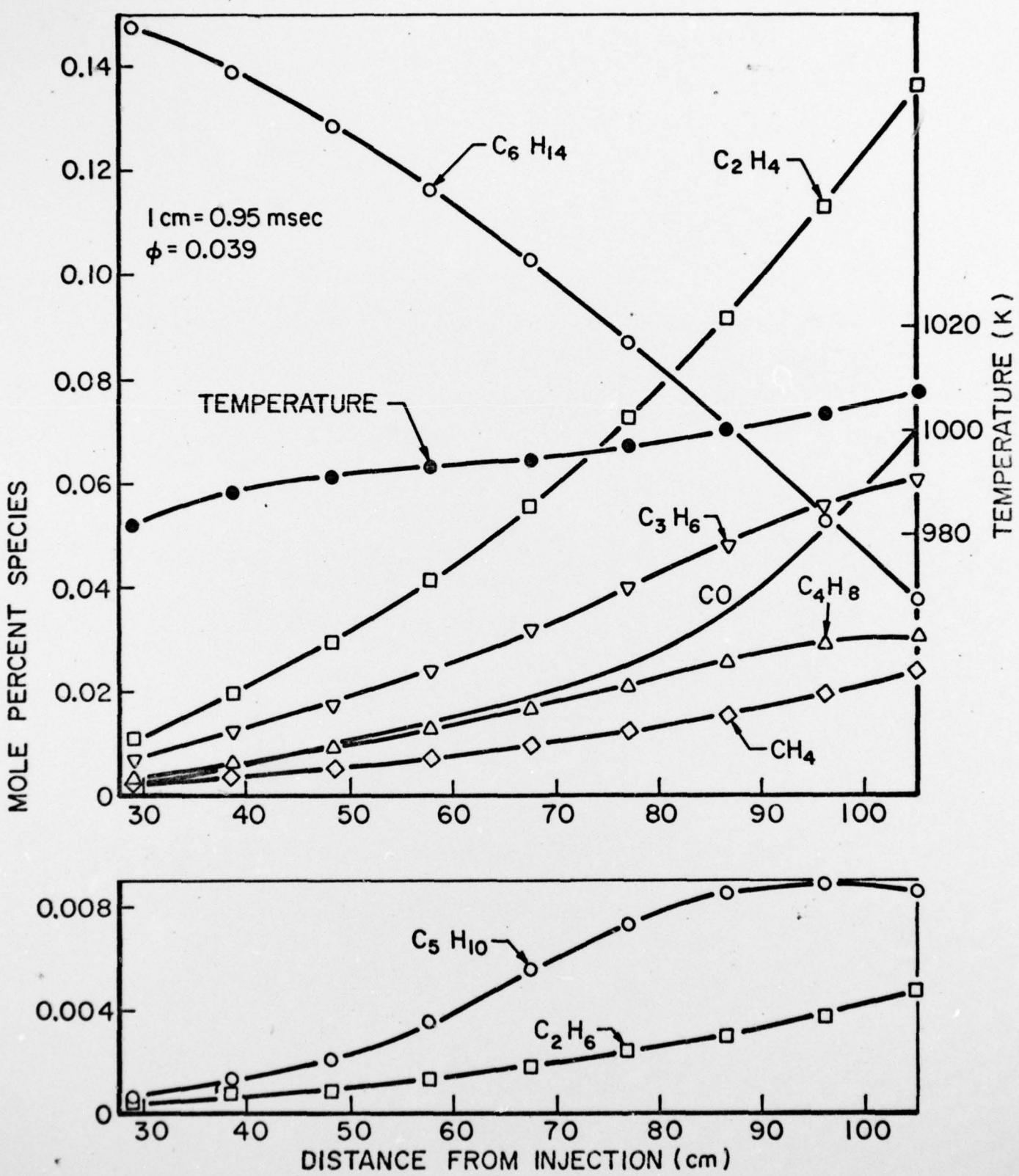
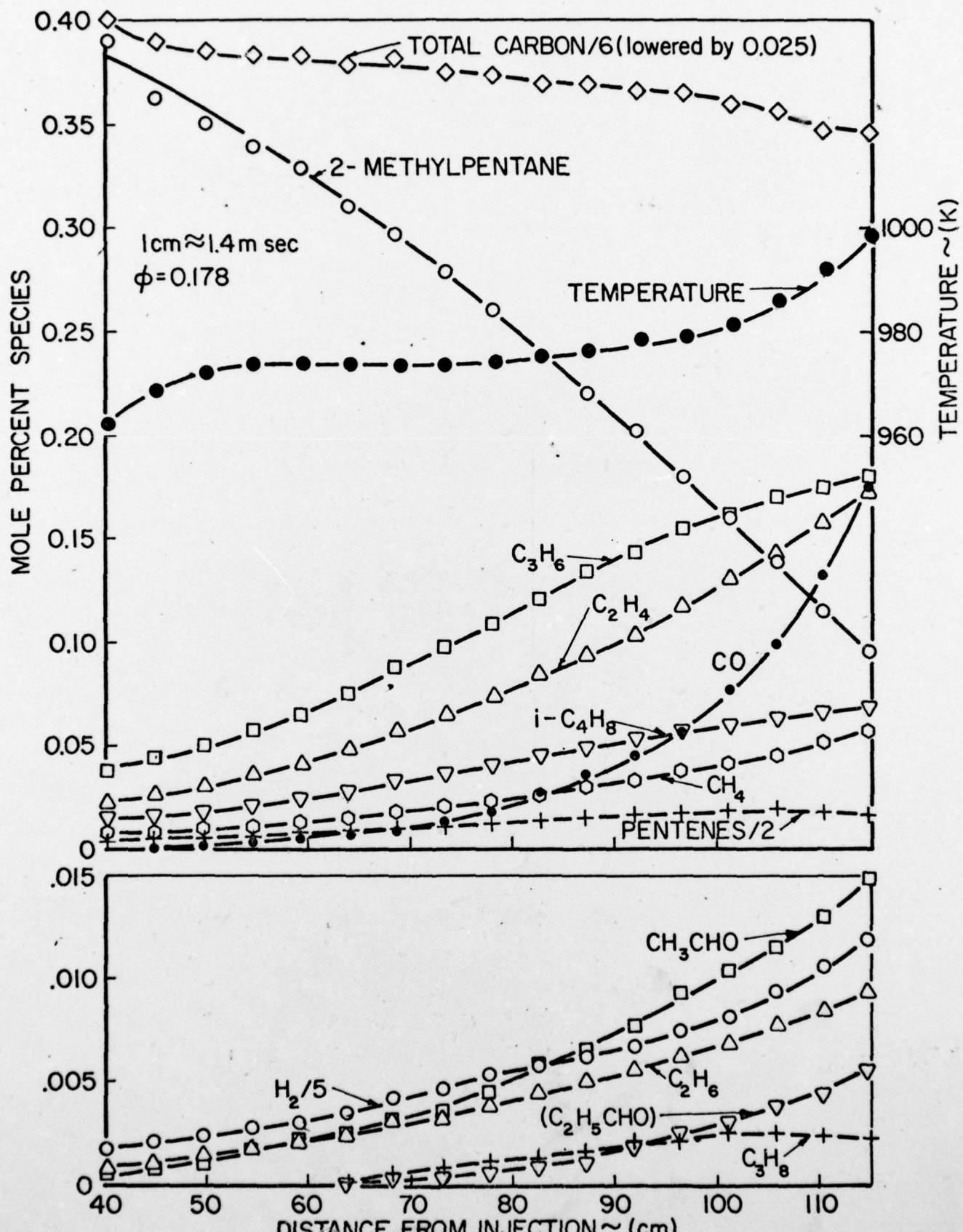


FIGURE 7



CHEMICAL COMPOSITION OF SPREAD  
2-METHYLPENTANE-AIR-REACTION

FIGURE 8

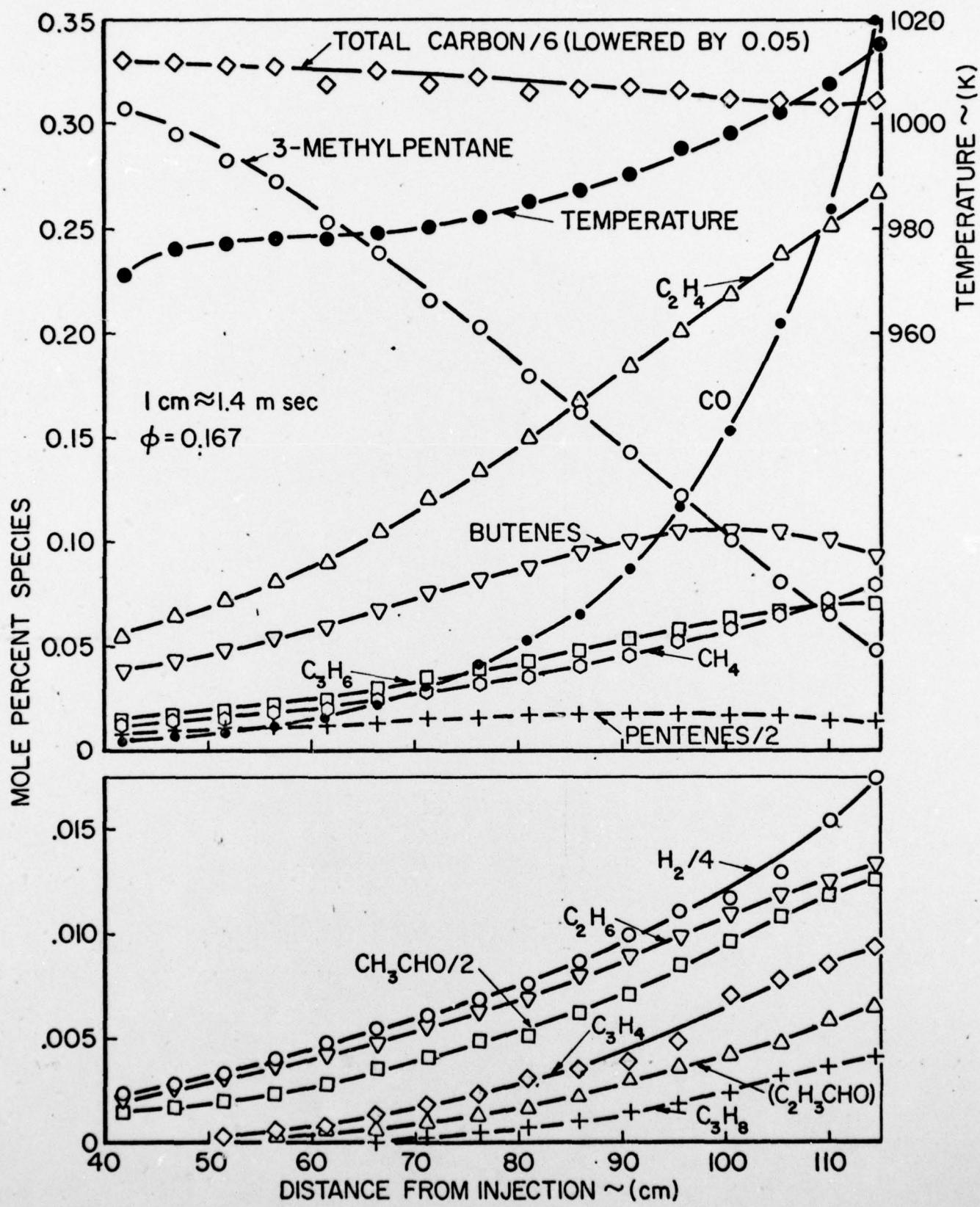


FIGURE 9

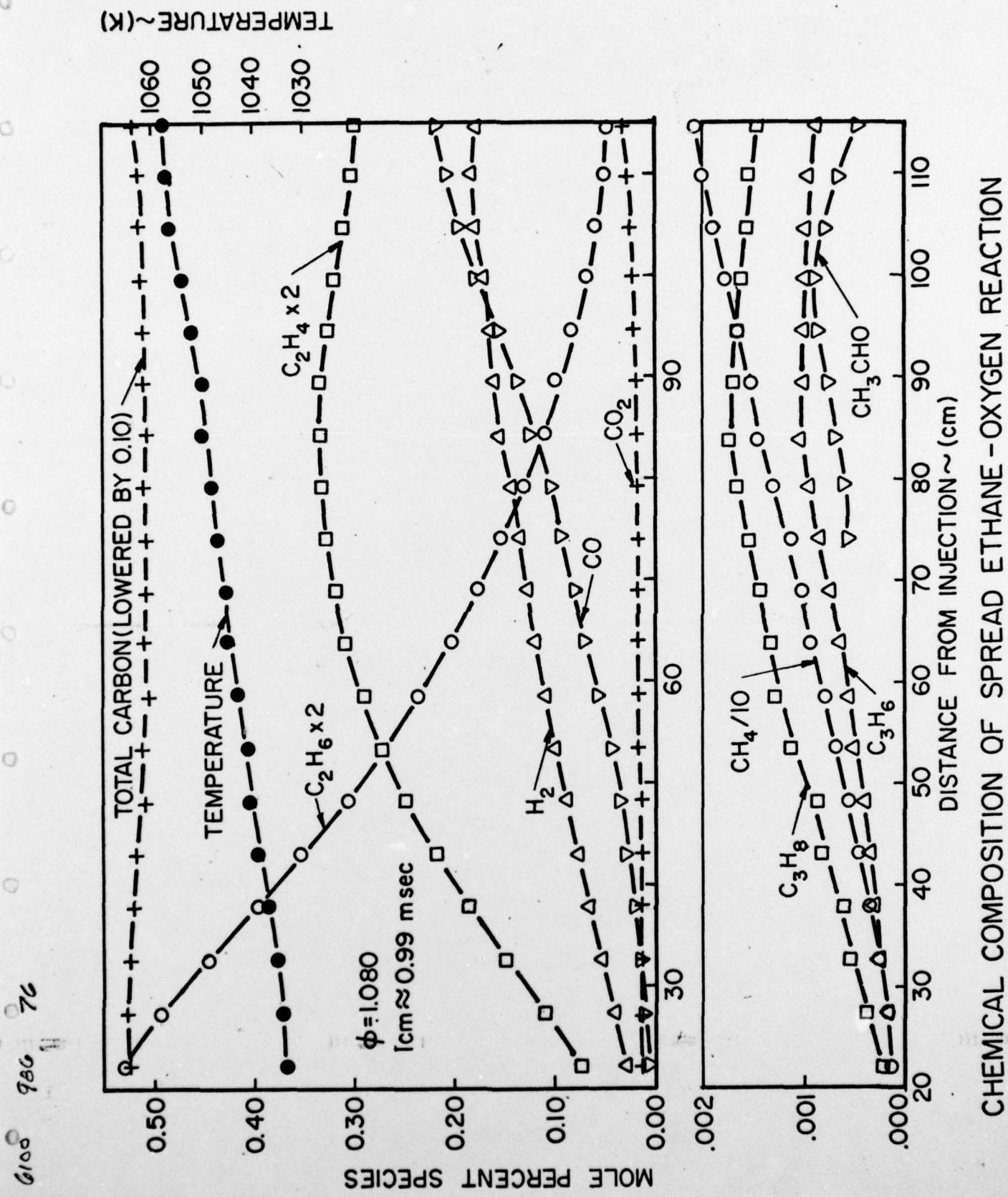
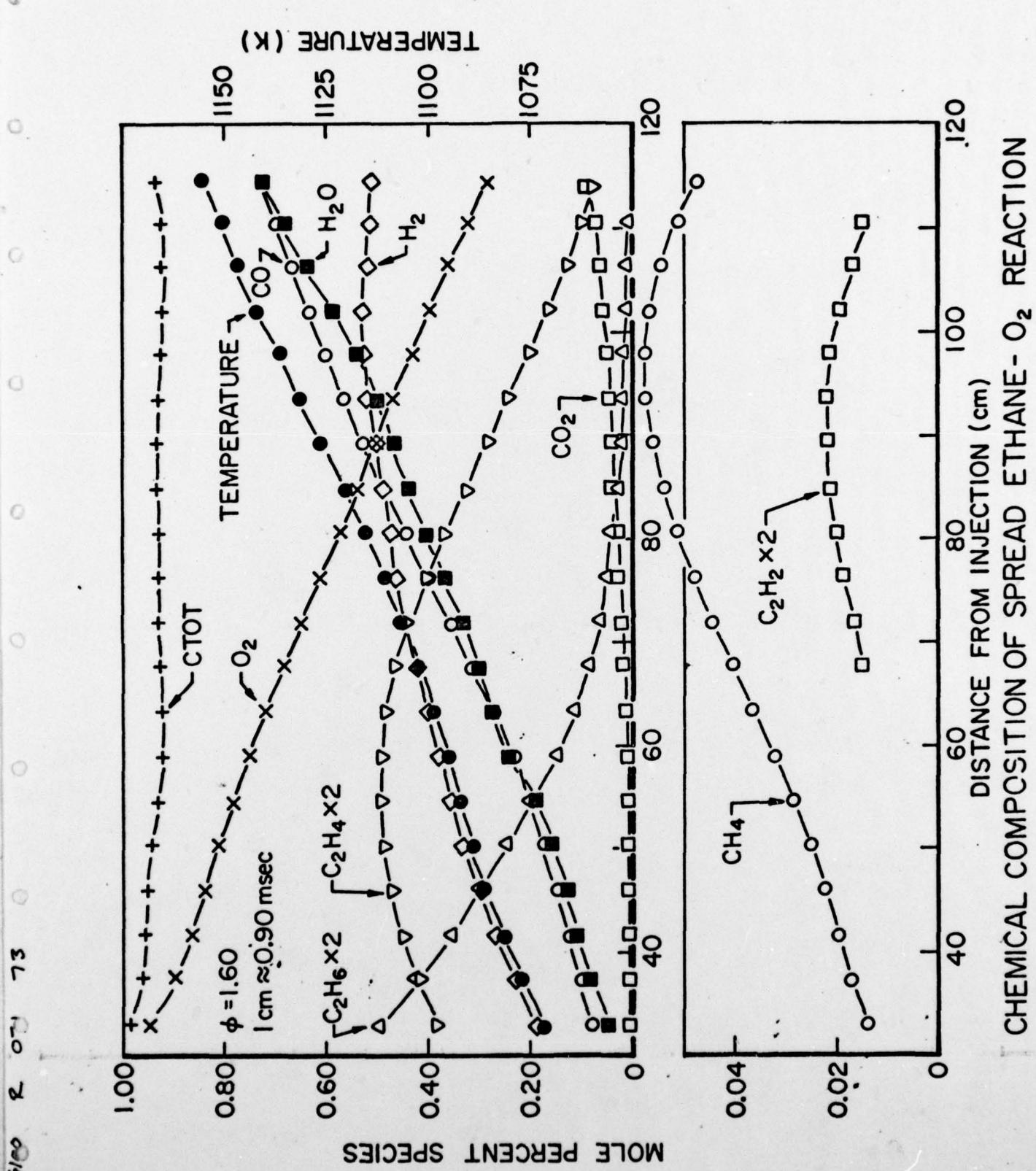
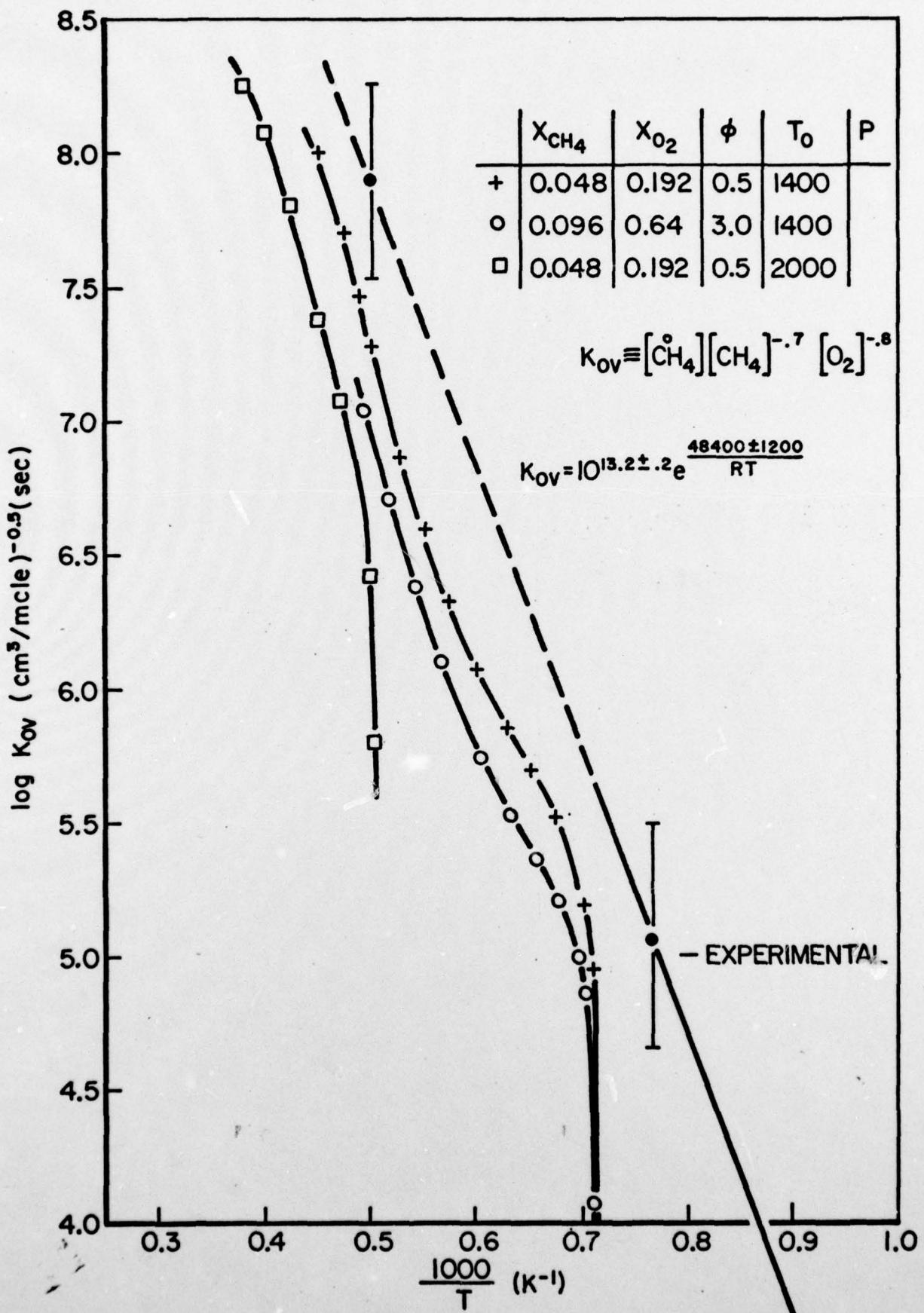


FIGURE 10

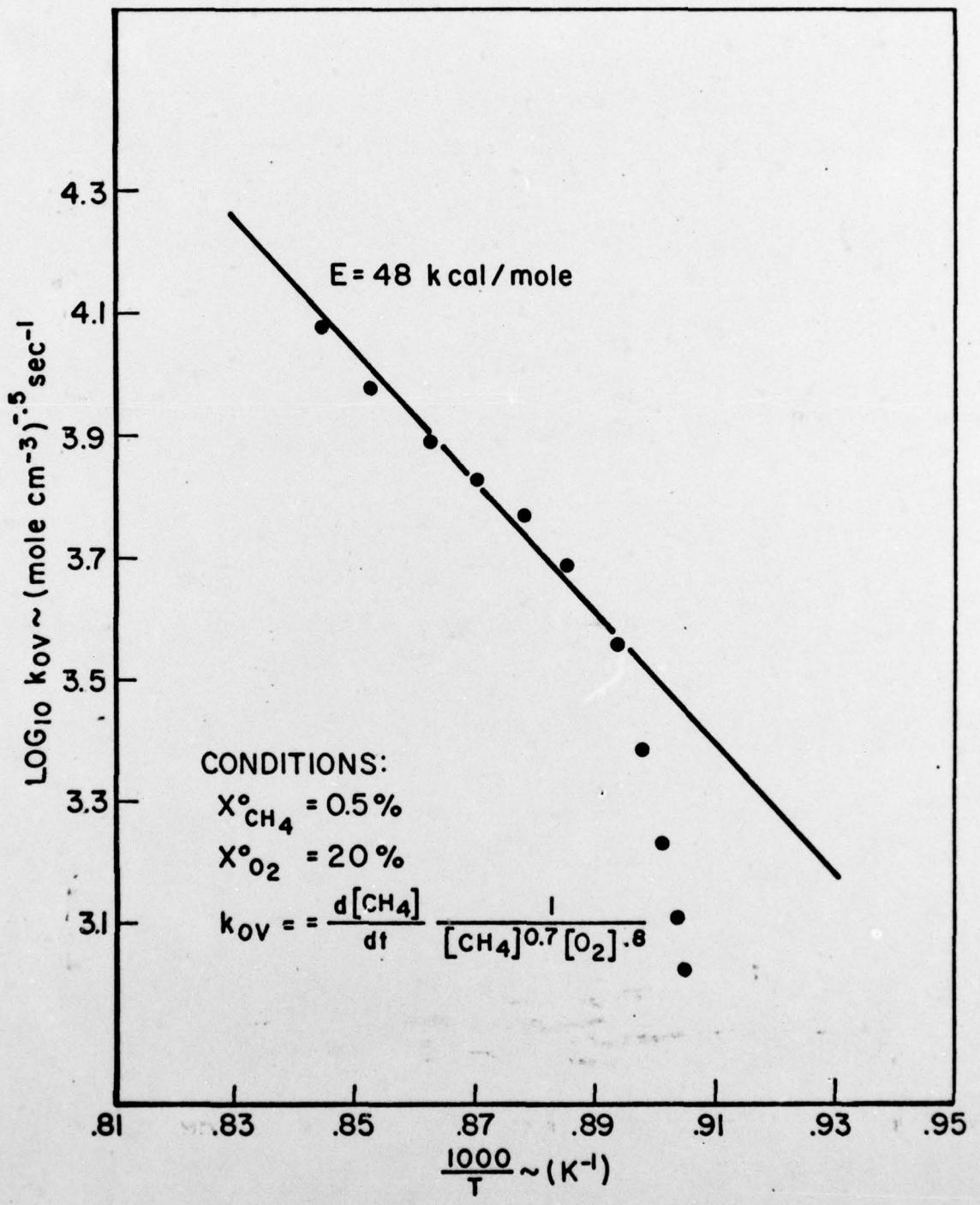
CHEMICAL COMPOSITION OF SPREAD ETHANE - OXYGEN REACTION





COMPARISON OF ANALYTICAL AND EXPERIMENTAL  
OVERALL DISAPPEARANCE RATE OF METHANE

FIGURE 12



DETERMINATION OF E FOR REACTION OF  $\text{CH}_4/\text{O}_2$

FIGURE 13

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>(18) AFOSR-TR-78-0061</b>	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) <b>OXIDATION KINETICS OF HYDROCARBON FUELS</b>		5. TYPE OF REPORT & PERIOD COVERED <b>FINAL rept. 1 Oct 73 - 30 Sep 77</b>
6. AUTHOR(s) <b>I GLASSMAN F L DRYER R J SANTORO</b>		7. PERFORMING ORG. REPORT NUMBER <b>AMS-13591</b>
8. CONTRACT OR GRANT NUMBER(s) <b>✓AFOSR-74-2604</b>		9. PERFORMANCE ORGANIZATION NAME AND ADDRESS <b>PRINCETON UNIVERSITY Dept. of Aerospace + Mech ✓ GUGGENHEIM AEROSPACE PROPULSION LAB Sciences PRINCETON, NEW JERSEY 08540</b>
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>2308B2 61102F</b>		11. CONTROLLING OFFICE NAME AND ADDRESS <b>AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332</b>
12. REPORT DATE <b>11 Dec 77</b>		13. NUMBER OF PAGES <b>12 / 48 p.</b>
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) <b>UNCLASSIFIED</b>
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>CHEMICAL KINETICS TURBULENT FLOW REACTOR HYDROCARBON FUELS OXIDATION KINETICS CHEMICAL LASERS FROM METALS COMBUSTION SYSTEMS</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  This report discusses interim results on the elucidation of high temperature oxidation kinetics of hydrocarbon fuels through experimental studies in a turbulent flow reactor. The report details current results particularly on ethane oxidation. Also discussed are results of an exploratory study of low pressure metal/oxidizer flame systems as a source of chemical laser action.		

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